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APPLICATION OF CONTINUOUS THERMODYNAMICS TO THE STABILITY OF POLYMER SYSTEMS. IV

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ABSTRACT

A method for establishing in the framework of continuous thermodynamics the stability criteria for multiple critical states of increasing order is presented. The method applies to a relatively general class of Gibbs free energy relations for polymer solutions: The function replacing the χ-term in the classic Flory-Huggins theory is permitted to depend on a finite number of moments of the polymer distribution so as to embrace most Gibbs free energy relations used in practice. In this way, determinant criteria for multiple critical states are formulated that are analogous in structure to those in traditional (discrete) thermodynamics. However, the dimension of the determinants is reduced from N (number of polymer species) to n (number of moments taken into account).

INTRODUCTION

The well-known determinant criterion for an m-fold critical point in an N + 1 component system reads (compare, e.g., [1]):

$$\begin{aligned} &D_j = 0; \qquad j = 0, \ldots, m \\ &D_{m+1} \neq 0 \end{aligned} \tag{1}$$

where the determinant D_0 is given by

$$D_0 = \begin{vmatrix} \partial^2 G/\partial X_1^2 & \partial^2 G/\partial X_1 \partial X_2 & \cdots & \partial^2 G/\partial X_1 X_N \\ \partial^2 G/\partial X_2 \partial X_1 & \partial^2 G/\partial X_2^2 & \cdots & \partial^2 G/\partial X_2 \partial X_N \\ \text{— — — —} & \text{— — — —} & \text{— —} & \text{— — — —} \\ \partial^2 G/\partial X_N \partial X_1 & \partial^2/\partial X_N \partial X_2 & \cdots & \partial^2 G/\partial X_N^2 \end{vmatrix} \tag{2}$$

and the other determinants result successively from

$$D_j = \begin{vmatrix} \partial D_{j-1}/\partial X_1 & \partial D_{j-1}/\partial X_2 & \cdots & \partial D_{j-1}/\partial X_N \\ \partial^2 G/\partial X_2 \partial X_1 & \partial^2 G/\partial X_2^2 & \cdots & \partial^2 G/\partial X_2 \partial X_N \\ \text{— — — —} & \text{— — — —} & \text{— —} & \text{— — — —} \\ \partial^2 G/\partial X_N \partial X_1 & \partial^2 G/\partial X_N \partial X_2 & \cdots & \partial^2 G/\partial X_N^2 \end{vmatrix} ; j = 1, 2, \ldots \tag{3}$$

Here G is the molar Gibbs free energy and $X_1, X_2, \ldots, X_N$ are the independent mole fractions of the system ($X_0 + X_1 + \ldots + X_N = 1$). For polymer solutions, it is more convenient to imagine all molecules to be divided into segments of equal size and to use segment-molar quantities instead of molar ones. Substituting in Eqs. (2) and (3) the segment-molar Gibbs free energy $\overline{\overline{G}}$ for G and the independent segment fractions $\psi_1, \psi_2, \ldots, \psi_N$ for $X_1, X_2, \ldots, X_N$, the critical point criterion retains the form of Eq. (1). The main problem in treating polymer solutions is the size of the determinants because, owing to the polydispersity of all synthetic polymers, N is a very large number.

This paper aims at reducing the problem to the case where, in the classic Flory-Huggins expression for $\overline{\overline{G}}$, the χ-term is replaced by a function $\overline{\overline{G}}^E$ according to (R-gas constant, T-temperature, P-pressure)

$$\frac{\overline{\overline{G}}^E}{RT} = \Gamma(T, P, \bar{r}_1, \ldots, \bar{r}_n) \tag{4}$$

i.e., where $\overline{\overline{G}}^E$ depends on the polymer distribution only by n moments

$$\bar{r}_i = \sum_{j=1}^{N} r_j^{k_i} \psi_j; \qquad i = 1, 2, \ldots, n \tag{5}$$

Here r_j is the segment number, and the exponents k_i are real numbers.

Fundamental investigations of this problem were published by Irvine and Gordon [2], who showed that, in this case, D_0 and D_1 also depend only on a limited number of moments. In this way, the dimension of the determinants to be considered could be reduced drastically by transition to an equivalent thermodynamic system possessing the same values of those moments that are necessary for calculating the critical state [3, 4]. The present authors [5, 6], on the basis of continuous thermodynamics, formulated determinants with the dimension n, $|Q|$, and $|Q_1|$, characterizing the critical states of polymer solutions. These considerations could be generalized to the critical states of polymer blends [7].

In these papers the question was not discussed whether the critical point considered is a simple or a multiple one or whether or not it is stable. Important results on these problems were presented by Šolc et al. [8, 9] restricted to the Flory-Huggins model; i.e., Γ depends on only one moment $\bar{r}_1$, the zero-th moment ($k_1 = 0$): $\overline{\overline{G}}^E/$

$RT = \Gamma(T,P,\psi_0) = \chi(T,P)\psi_0(1 - \psi_0)$. This model was also the first one which was generalized to polydisperse polymer solutions in the framework of continuous thermodynamics [1].

In the present paper the technique used there and in [10] for establishing successively the stability criteria for multiple critical states with increasing order will prove to be suitable for generalization to a continuous treatment. Three equivalent criteria for multiple critical states—a transformation criterion, a variation criterion, and a determinant criterion—will be considered on the discrete basis. But only the second one may easily be transformed to continuous thermodynamics, which is based on the direct application of a continuous distribution density function $W(M)$ in the thermodynamic calculations. Here $W(M)\,dM$ gives the relative segment fraction of all polymer species with segment numbers between M and $M + dM$. After neglecting linear terms, $\overline{\overline{G}}$ in continuous thermodynamics is given by

$$\frac{\overline{\overline{G}}}{RT} = \frac{\psi_0 \ln \psi_0}{r_0} + \int \frac{\psi W \ln (\psi W)}{r}\,dM + \Gamma \tag{6}$$

where ψ_0 and r_0 are segment fraction and segment number of the solvent, respectively, ψ is the overall segment fraction of the polymer, and $r = r(M)$ is the segment number of the polymer species identified by M. In this paper all integrals are to be taken over the total occurring M-interval. Of course, in continuous thermodynamics the moments are given by

$$\bar{r}_i = \int r^{k_i} \psi W\,dM; \qquad i = 1, 2, \ldots, n \tag{7}$$

To avoid thrusting the thermodynamic relations into the background by presenting voluminous mathematical proofs, only the outline of the mathematical derivations will be given. The interested reader will find the details in [11].

DISCRETE TREATMENT

In the discrete case, higher-order stability criteria possess many common features with extremum conditions sufficient for functions of several variables: A stable or metastable critical point corresponds to a degenerate local minimum of $\overline{\overline{G}}$. In this section such extreme conditions will be developed; then the question arises whether they may be transformed to continuous thermodynamics.

By means of the transformation

$$h_i = \lambda_i h_1^{(1)} + (1 - \delta_{1i})h_i^{(1)} \text{ with } h_i = d\psi_i (i = 1, \ldots, N) \tag{8}$$

(where $\delta_{ij} = 1$ if $i = j$ and $\delta_{ij} = 0$ otherwise), we showed [10] that the sign of the Taylor expansion of $\overline{\overline{G}}$ up to fourth-order terms depends, near the critical point, on the sign of a quadratic form of the quantities $h_1^{(1)^2}, h_2^{(1)}, \ldots, h_n^{(1)}$ leading to a sufficient stability criterion for a simple stable critical point in the form $D_0 = 0$, $D_1 = 0$, $D_2 > 0$. For $D_2 < 0$ it is a simple unstable critical point, and for $D_2 = 0$ a multiple critical point.

In this paper the multiplicity and the stability will be studied. To this end, the higher-order partial derivatives of $\overline{\overline{G}}$ at the critical point are needed. For brevity, the following symbols are introduced

$$a(\nu) = a(\nu,\psi) = \frac{\partial^{|\nu|}\overline{\overline{G}}(T,P,\psi_1, \ldots, \psi_N)}{\partial\psi_1^{\nu_1} \ldots \partial\psi_N^{\nu_N}} \tag{9}$$

where ν is a multi-index $\nu = (\nu_1, \ldots, \nu_N)$ with $|\nu| = \sum_{i=1}^{N} \nu_i$, and ψ means (only in this section) the vector of independent mole fractions $\psi = (\psi_1, \ldots, \psi_N)$. Using the unit vectors $e_p = (0, \ldots, 1, 0, \ldots, 0)$ ($p = 1, \ldots, N$; 1 is situated at the p-th position), we may write $\nu = \sum_{p=1}^{N} \nu_p\, e_p$. In this way, e.g., the derivative $\partial^{|\nu|}\, \overline{\overline{G}}(T,P,\psi_1, \ldots, \psi_N)/\partial\psi_1^3\, \partial\psi_4$ becomes a $(3e_1 + e_4, \psi)$. The general stability criterion is formulated in terms of the symmetrical matrices

$$A^{(k)} = \begin{pmatrix} \binom{2k+1}{k}^{-1} a^{(k)}((2k+2)e_1) & a^{(k)}((k+1)e_1 + e_2) & \cdots & a^{(k)}((k+1)e_1 + e_N) \\ a^{(k)}((k+1)e_1 + e_2) & a(2e_2) & \cdots & a(e_2 + e_N) \\ a^{(k)}((k+1)e_1 + e_N) & a(e_2 + e_N) & \cdots & a(2e_N) \end{pmatrix} \tag{10}$$

Here $a^{(0)} = a$ (i.e., $A^{(0)}$ equals the matrix of the second-order partial derivatives) and $a^{(k)}(\nu)$ may be calculated successively according to the formula

$$a^{(k)}(\nu) = \sum \frac{\nu_i!}{(\nu_1 - k\,|\tau|)!\tau!} \prod_{j=2}^{N} \left(\frac{\lambda_j^{(k-1)}}{k!\lambda_1}\right)^{\tau_j} a^{(k-1)}(\nu + \tau - k|\tau|e_1), \tag{11}$$

where the summation is to be taken over all indexes $\tau = (0,\tau_2, \ldots, \tau_N)$ obeying $\nu_1 - k|\tau| \geq 0$. Furthermore, $\lambda_j^{(k-1)} = (-1)^{j+1}\, |A_j^{(k-1)}|$, and $A_j^{(k-1)}$ means the matrix obtained from $A^{(k-1)}$ by neglecting the first row and the j-th column; i.e., $\lambda_j^{(k-1)}$ is the cofactor of $a^{(k-1)}(ke_1 + e_j)$ in $A^{(k-1)}$. Finally, $\lambda_i^{(0)} = \lambda_i$ and $\tau! = \Pi_{i=2}^{N} \tau_i!$. In this paper the assumption is made that all functions are differentiable as often as needed to calculate the needed expressions.

The quantity decisive for stability considerations is the nonlinear part of the segment-molar Gibbs free energy $\overline{\overline{G}}$. Designating the critical composition by ψ^0 and introducing

$$\Delta\overline{\overline{G}} = \overline{\overline{G}}(\psi) - \overline{\overline{G}}(\psi^0) - \nabla\overline{\overline{G}}(\psi^0)(\psi - \psi^0) \tag{12}$$

the stability criterion may be expressed in the following form:

Criterion I: *If (1)* $A_l^{(0)}(\psi^0)$ *is positive definite,*
(2) $|A^{(k)}(\psi^0)| = 0$ *for* $k = 0, 1, \ldots, m - 1$,
(3) $a^{(k)}((2k + 1)e_l; \psi^0) = 0$ *for* $k = 0, 1, \ldots, m$, *and*
(4) $|A^{(m)}(\psi^0)| > 0$,
then there exists a region around ψ_0 *such that*
$\Delta\overline{\overline{G}} > 0$ *for all* $\psi \neq \psi^0$ *within this region;*
i.e., ψ^0 *is a local minimum point of* $\Delta\overline{\overline{G}}$.

In the language of thermodynamics, this means that in ψ^0 a $(2m - 1)$-fold stable critical state exists. Due to the complexity of the recursion formula Eq. (11), this criterion is not convenient for the user. Therefore, equivalent and more convenient statements were derived. To this end, the determinant $|A^{(0)}(\psi)|$ is expanded with respect to the first row, $d_0(\psi) = \Sigma_{i=1}^{N} \lambda_i a(e_1 + e_i; \psi)$, and the directional derivatives in the direction given by the vector $l = (\lambda_1, \ldots, \lambda_N)$ are calculated successively. This leads to

Criterion II: *Eqs. (2), (3), (4) in Criterion I are equivalent to*
(IIa) $d_k(\psi^0) = 0$ *for* $k = 0, 1, \ldots, 2m + 1$
(IIb) $d_{2m+2}(\psi^0) > 0$

Finally, there is a third way of calculating based on consideration of the following determinants

$$D_0(\psi) = |A^{(0)}(\psi)|$$

$$D_{j+1}(\psi) = \begin{vmatrix} \dfrac{\partial D_j(\psi)}{\partial \psi_1} & \cdots & \dfrac{\partial D_j(\psi)}{\partial \psi_N} \\ a(e_2 + e_1) & \cdots & a(e_2 + e_N) \\ \hline a(e_N + e_1) & \cdots & a(2e_N) \end{vmatrix} \tag{13}$$

Then the criterion is

Criterion III: *Eqs. (2), (3), (4) in Criterion I are equivalent to*
(IIIa) $D_k(\psi^0) = 0$ *for* $k = 0, 1, \ldots, 2m + 1$
(IIIb) $D_{2m+2}(\psi^0) > 0$

Whereas the equivalency of Criteria II and III may easily be shown by induction, the proof of the equivalency of Criteria I and II needs wider algebraic reformulations, including remarks 4.1-4.3 in [12].

The following points are important to permit the transition to the continuous case:

$-d_{i+1}(\psi)$ may be calculated as a simple differential in the direction l (Gateaux differential), i.e.,

$$d_{i+1}(\psi) = \lim_{t\to 0} \frac{d_i(\psi + tl) - d_i(\psi)}{t} = \delta d_i(\psi; l); \tag{14}$$

d_0 equals the second differential of $\overline{\overline{G}}/RT$, i.e.,

$$d_0(\psi) = \delta^2\overline{\overline{G}}(\psi; l)/RT \tag{15}$$

– For A_1 – positive definite, $|A| = 0$ the vector l introduced above may be characterized in the following way: If $s(h) = \Sigma_{i,j=1}^{N} a(e_i + e_j)\, h_i h_j$, then the relation

$$\min s(h) = s(h^0) \tag{16}$$

holds if and only if a number α exists obeying $h^0 = \alpha l$.

CONTINUOUS TREATMENT

This section aims at establishing by continuous thermodynamics a criterion for stable critical states of polymer solutions described by momentum-dependent $\overline{\overline{G}}_E$-relations. The last two remarks of the preceding section permit the transformation of Criterion II to the continuous case where $\overline{\overline{G}}$ is given by Eq. (6). As shown earlier [6], $d(\psi W)^0 = -r(M)\psi W(M)\ \Sigma_{i,j=1}^n r(M)^{k_i} c_{ij} y_j^0$ now bears the minimum property of Eq. (16), resulting in

$$\delta^2 \frac{\overline{\overline{G}}}{RT} (T,P,\psi W;d(\psi W)^0) = 0 \tag{17}$$

Here y^0 is the solution of $Qy = 0$ (under the assumption rank $Q = n - 1$, Q-positive semidefinite) with

$$\begin{aligned} Q &= \overline{R}^{-1} + C, C = (c_{ij})_{i,j=1}^n, c_{ij} = \partial^2\Gamma'/(\partial\overline{r}_i\partial\overline{r}_j),\Gamma' = \Gamma + \psi_0 r_0^{-1} \ln \psi_0 \\ \overline{R} &= (\overline{r}_{i,j})_{i,j=1}^n, \overline{r}_{ij} = \int (r(M))^{k_i} + {}^{k_j+1}\ \psi W(M)\, dM \end{aligned} \tag{18}$$

Furthermore, the elements of the matrix $\overline{R}^{-1}$, which is the inverse of $\overline{R}$, will be designated by $\hat{r}_{ij}$. In Eq. (18) ψ_0 and ψ are the segment fraction of the solvent and the overall segment fraction of all polymer species, respectively; r_0 and r are the segment number of the solvent and of the individual polymer species, respectively; W is the normalized and $\psi\ W$ the nonnormalized distribution density function of the polymer, M designates the polymer species.

Without restricting the generality, the matrix $\overline{Q}$, which is obtained from Q by neglecting the first row and the first column, may be assumed to have full rank: $|\overline{Q}| \neq 0$. In this way the vector y^0 may be considered to be a function of ψW in a certain region around the spinodal point investigated, and generally we may write $Qy = \alpha\ (|Q|/|\overline{Q}|, 0, \ldots, 0)^T$ with α arbitrarily real. According to $Q = \overline{R}^{-1} + C$, the quantity $d(\psi W)^0$ may be written as $d(\psi W)^0 = r(M)\psi W(M)\ \Sigma_{i,j=1}^n (r(M))^{k_i}\hat{r}_{ij}y_j^0$.

This equality holds exactly for the spinodal points. In their regions discussed above, the term $-\alpha r(M)\psi W(M)\ |Q|/|\overline{Q}|$ has to be added on the right-hand side. This term vanishes at the spinodal for multiple critical points, including a certain number of variations in the point investigated. Hence, for stability considerations, this additional term may be neglected. In this way we obtain

$$\delta^2 \frac{\overline{\overline{G}}}{RT} (\psi W;d(\psi W)^0) = \sum_{i,j=1}^{n} q_{ij}\, y_i^0\, y_j^0 = <Qy^0,y^0> = f_0(\psi W) \tag{19}$$

f_0 corresponds to d_0 in the discrete case.

In an earlier paper [6] the critical point was calculated by means of the relation $\delta^3\overline{\overline{G}}/RT\ (\psi W;d(\psi W)^0) = 0$ since it could be shown that for all ψW obeying $|Q(\psi W)| = 0$ this relation applies if and only if $|Q_1| = 0$. This statement may be included in the general treatment by showing that for all ψW obeying $|Q(\psi W)| = 0$ the equivalency applies: $f_1(\psi W) = \delta f_0(\psi W;d(\psi W)^0) = 0$ if and only if $|Q_1| = 0$. Indeed, forming the first differential of f_0 with respect to $d(\psi W)^0$ we obtain $\delta f_0 = <\delta Q y^0, y^0> + 2<Qy^0,\delta y^0>$. (To abbreviate, in differentials with respect to $d(\psi W)^0$ from now on the increase will not be specified explicitly). Since $<Qy^0,\delta y^0> = (\alpha|Q|/|\overline{Q}|)\delta\alpha \equiv 0$ and $\delta\hat{r}_{ij} = -\Sigma_{p,d,e,f}^n \overline{r}_{def}\hat{r}_{id}\hat{r}_{je}\hat{r}_{pf}y_p^0$ (according to $\overline{R}\,\overline{R}^{-1} = I$ and, hence, $\delta\overline{R}^{-1} = -\overline{R}^{-1}\delta(\overline{R})\overline{R}^{-1}$), we obtain with $\delta c_{ij} = \Sigma_{p=1}^n c_{ijp}y_p^0$

$$f_1(\psi W) = \sum_{i,j,p=1}^{n} \left(c_{ijp} - \sum_{d,e,f=1}^{n} \bar{r}_{def}\hat{r}_{id}\hat{r}_{je}\hat{r}_{pf}\right) y_i^0 y_j^0 y_p^0 \tag{20}$$

According to [6], at the spinodal the right-hand side may also be written in the form $\alpha^3 \, |Q| / |\overline{Q}|^2$ proving the statement.

For further considerations the differential δf_1 is important, reading

$$f_2(\psi W) = \delta f_1 = \frac{3}{|\overline{Q}|} \begin{vmatrix} \frac{1}{3}\, q_{1111}^{(1)} & q_{112}^{(1)} & \cdots & q_{11n}^{(1)} \\ q_{112}^{(1)} & & & \\ \vdots & & \overline{Q} & \\ q_{11n}^{(1)} & & & \end{vmatrix} \tag{21}$$

with $q_{1111}^{(1)} = \sum\limits_{i,j,p,k=1}^{n} q_{ijpk} \, y_i^0 y_j^0 y_p^0 y_k^0$, $q_{11k}^{(1)} = \sum\limits_{i,j=1}^{n} q_{kij} \, y_i^0 y_j^0$

where $q_{ijp} = \hat{r}_{ijp} + c_{ijpk}$ and $q_{ijpk} = \hat{r}_{ijpk} + c_{ijpk}$

with $\hat{r}_{ijp} = -\sum\limits_{d,e,f=1}^{n} \bar{r}_{def}\hat{r}_{id}\hat{r}_{je}\hat{r}_{pf}$

and $\hat{r}_{ijpk} = \sum\limits_{d,e,f,s=1}^{n} \left(-\bar{r}_{defs} + \sum\limits_{u,t=1}^{n} (\bar{r}_{deu}\bar{r}_{tfs} + \bar{r}_{dfu}\bar{r}_{tes} + \bar{r}_{efu}\bar{r}_{tds})\hat{r}_{ut}\right)\hat{r}_{id}\hat{r}_{je}\hat{r}_{pf}\hat{r}_{ks}$

Here the higher-order partial derivatives of the (extended) function Γ' occur, i.e., $c_{i_1,\ldots,i_s} = \partial^s\Gamma'/(\partial\bar{r}_{i_1} \ldots \partial\bar{r}_{i_s})$, and the higher-order moments $\bar{r}_{i_1,\ldots,i_s} = \int r_{r}^{k_{i_1}+\ldots+k_{i_s}+s-1} \psi W \, dM$. On this basis, the following sufficient stability criterion for critical states of polymer solutions may be derived:

Stability Criterion: *If Q-positive semidefinite, rank $Q = n - 1$*
and if (1) $f_0 = 0$, (2) $f_1 = 0$,
(3) $f_2 > 0$ then the thermodynamic system is stable or metastable at the critical point.

The form of this criterion is similar to considerations of the discrete case (e.g., compare f_i and d_i). In an analogous way it may be shown that Criterion III also has an equivalent for momentum-dependent excess parts. Let us define matrices Q_i by

$$Q_i = \begin{pmatrix} \dfrac{D|Q_{i-1}|}{D\bar{r}_1} & \cdots & \dfrac{D|Q_{i-1}|}{D\bar{r}_n} \\ q_{21} & \cdots & q_{2n} \\ - - - & - - - & - - - \\ q_{n1} & \cdots & q_{nn} \end{pmatrix}; \; Q_0 = 0 \tag{22}$$

Here the D-derivative of the determinant $|Q_{i-1}|$ is to be performed in columns applying $\dfrac{Dq_{ij}}{D\bar{r}_p} = q_{ijp}$, $\dfrac{Dq_{ijp}}{D\bar{r}_k} = q_{ijpk}$ etc. Then the equivalent criterion becomes

Eqs. (1), (2), (3) in the Stability Criterion are
equivalent to (1) $|Q| = 0$, *(2)* $|Q_1| = 0$, *(3)* $|Q_2| > 0$

So far, criteria for *simple* critical states have been derived. However, the method presented here also permits the successive formulation of sufficient determinant criteria for higher-order critical states. Starting with $|Q_2| = 0$ or $f_2 = 0$, the quantities $\delta f_2 = f_3$ and $\delta f_3 = f_4$ may be calculated. If $f_3 = 0$ and $f_4 > 0$, then the multiple critical point may be shown to be stable or metastable. In analogy to f_2, determinants corresponding to f_3 and f_4 may be formulated:

$$f_3 = \frac{\alpha^5}{|Q|^4}|Q_3| \; ; \qquad f_4 = \frac{\alpha^6}{|Q|^5}|Q_4| \tag{23}$$

Successive derivations lead to the following general and sufficient criterion:

General Stability Criterion: *If Q-positive semidefinite,*
rank $Q = n - 1$ *and if*
(1) $|Q_j| = 0$ $(j = 0, 1, \ldots, 2m - 1)$
(2) $|Q_{2m}| > 0$ *(m – positive, integer)*
then the $(2m - 1)$ *fold critical point*
is stable or metastable

Defining the derivative $D/D\bar{r}_i$ for momentum-dependent excess parts in an appropriate way, this criterion reproduces the form of Criterion III. This enables us to consider n-rowed determinants (typically n is not larger than 5) instead of N-rowed determinants (usually N is of the order of 1000). In this way the computing expense and numerical problems (rounding errors) are reduced drastically, especially if all the moments may be calculated analytically.

DISCUSSION

The question is how many moments of the distribution density function ψW are needed to apply the criteria $|Q_s| = 0$ (or > 0) if Γ' contains n different moments. Obviously, the answer depends on which moments influence Γ'. To point this out more clearly, let us define $\bar{r}_i$ in this subsection by

$$\bar{r}_i = \int r^i \, \psi W \, dM; \qquad i = 1, 2, \ldots, n \tag{24}$$

The answer to our question becomes simple for $n = 1$: In this case $\Gamma' = \Gamma'(\bar{r}_0)$ resulting in $Q_s = Q_s(\bar{r}_0, \bar{r}_1, \ldots, \bar{r}_{s+1})$; i.e., Q_s depends on $s + 2$ different moments. In a similar simple way the cases $\Gamma' = \Gamma'(\bar{r}_0, \ldots, \bar{r}_n)$, $\Gamma' = \Gamma'(\bar{r}_0, \bar{r}_{-1}, \ldots, \bar{r}_{-n})$, and $\Gamma' = \Gamma'(\bar{r}_{-1}, \bar{r}_0, \bar{r}_1, \ldots, \bar{r}_n)$, $n \geq 1$, may be treated. The results are $Q_s = Q_s(\bar{r}_0, \bar{r}_1, \ldots, \bar{r}_{s(n+1)+2n+1})$, $Q_s = Q_s(\bar{r}_{s+1}, \bar{r}_s, \ldots, \bar{r}_{-(s+2)(n-1)-1})$, and $Q_s = Q_s(\bar{r}_{-1}, \bar{r}_0, \ldots, \bar{r}_{(s+2)n+s+1})$, respectively; i.e., Q_s depends on $(s + 2)(n + 1)$, $(s + 2)n + 1$, and $(s + 2)(n + 1) + 1$ consecutive moments, respectively. Hence, the generalization of the truncation theorem dating back to Irvine and Gordon [2] reads:

If Γ' *depends on* $\bar{r}_0, \ldots, \bar{r}_n$ *then all thermodynamic systems with equal moments* $\bar{r}_0, \ldots, \bar{r}_{s(n+1)+2n+1}$ $(s > 1)$ *possess the same stability behavior in an* $(s - 1)$*-fold critical state.*

For a given number n of different moments $\bar{r}_k$ occurring in Γ', the maximum number of moments occurring in Q_s equals $\binom{n+s+2}{n} - 1$, as may easily be shown by induction. This number is reached, for example, if $\Gamma' = \Gamma'(\bar{r}_{k_1}, \ldots, \bar{r}_{k_n})$ with $k_t = \frac{(s+2)^t - 1}{s+1} - 1$, $(t = 1, \ldots, n)$. Thus, if Γ' depends on three moments, the number of moments necessary to establish the stability of a *simple* critical point ($s = 2$) varies between 9 (for $\Gamma' = \Gamma'(\bar{r}_{-1}, \bar{r}_0, \bar{r}_1)$) and, say, 34 (for $\Gamma' = \Gamma(\bar{r}_0, \bar{r}_4, \bar{r}_{20})$). For a threefold critical point ($s = 4$) these numbers are 13 and 83, respectively.

This example shows that the truncation method (i.e., replacing a multicomponent system by a system with a small number of components with the same values of the relevant moments) comes relatively soon to the bounds of practicality if multiple critical points are to be considered.

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